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*THE VELOCITY OF POLYMORPHIC CHANGES BETWEEN
SOLIDS.*

BY P. W. BRIDGMAN.

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(Continued from page 3 of cover.)

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THE VELOCITY OF POLYMORPHIC CHANGES BETWEEN SOLIDS.

By P. W. BRIDGMAN.

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In preceding papers ¹ I have presented complete data for a number of polymorphic transitions between solids under high pressures. It is well known, however, that data which may be complete from the point of view of thermodynamics may not be at all complete from other points of view, and therefore cannot be complete enough to determine the mechanism of a process. For example, a complete description of the thermodynamic behavior of a perfect gas gives no hold on the viscosity or the thermal conductivity. The kinetic theory of gases, however, which describes the mechanism, does account for viscosity and thermal conductivity as well as for the thermodynamic properties. A knowledge of other properties than those of thermodynamics is important, therefore, because of the additional light it may throw on the complete mechanism. In this paper additional data of this kind, data for the reaction velocity from one phase to another, are given for many of the substances for which the thermodynamic data have been given in preceding papers.

The plan of presentation is as follows. First, is given such description as may be necessary of experimental methods, the method of computation from the data, and the abbreviated graphical method by which an entire curve is represented by a single point. This will involve emphasis of two important facts, namely that there is a distinct region on both sides of the equilibrium point within which the reaction will not run, and that the reaction velocity varies according to the direction in which it is running, being almost always slower in that direction which is accompanied by rising pressure. The data for

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- 1 P. W. Bridgman. (A) Proc. Amer. Acad., 439-558 (1912).
(B) Phys. Rev., 126-141 and 153-202 (1914).
(C) Jour. Amer. Chem. Soc., **36**, 1344-1363 (1914).
(D) Phys. Rev., **6**, 1-33 and 94-112 (1915).
(E) Proc. Amer. Acad., **51**, 55-124 (1915).
(F) Proc. Nat. Acad., **1**, 513-516 (1915).
(G) Proc. Amer. Acad., **51**, 576-625 (1916).

Throughout the rest of this paper reference will be made to these papers by letter.

all the individual substances for which the data are now at hand will then be presented, and finally, the significance of the data and their suggestions as to a possible mechanism will be discussed.

METHODS.

The apparatus was the same as that which has already been described and most of the measurements were made at the same time as those of preceding papers. The only measurements made with this subject alone in view were a few on potassium chlorate. To every equilibrium point of the preceding papers there may correspond two velocity curves, giving the rate of reaction with rising and falling pressure. But in many cases it was not practicable to obtain these two curves, especially if the reaction were a rapid one or one accompanied by a small change of volume, so that the data given here are by no means so complete as the equilibrium data.

The following brief description of method applies to readings all at the same temperature. For definiteness we will suppose that we are measuring the rate at which the low pressure phase (I) changes to the phase stable at higher pressures (II). Pressure on I is first slowly increased until it has been carried so far into the region of stability of II that nuclei of II are formed spontaneously. After the formation of nuclei, the phase II grows at the expense of I by an advance of the surface of separation. The formation of II is accompanied by dropping of the pressure back toward the equilibrium line. The reason for this fall of pressure is, of course, that the phase stable at the higher pressure necessarily has the smaller volume. Since the fall of pressure is proportional to the change of volume, and therefore to the amount of I changed into II, the reaction velocity may be simply measured by measuring the rate at which pressure drops back. It is obvious that a precisely similar procedure gives the rate at which II changes to I, the pressure now rising as the reaction runs. These two sets of readings with rising and falling pressure are to be repeated at different temperatures.

For the measurements of time an ordinary watch was used, and the pressure was determined in the usual way by measuring with a Carey Foster bridge the resistance of a coil of manganin wire subjected to the pressure. The resistance was given by the position of the slider on the bridge wire, the setting being made for no galvanometer deflection. It can be well understood that this measurement

of pressure might consume a little time. I could not make a measurement of pressure, if all the adjustments had to be made, in much less than 15 seconds, but if I knew approximately what the pressure was, the measurement could be made in considerably less time. It was not possible, therefore, to make accurate measurements when the pressure was rapidly changing, and if the transition were very rapid, as that between ice I and III near the triple point with the liquid,² it was not possible to make any measurements at all. On the other hand, if the reaction is slow, it is possible to make the readings as accurately as the time can be read from the second hand of an ordinary watch, that is, to within perhaps one second. This is accomplished by setting the slider at a definite mark and keeping the key pressed down. As the pressure changes with time the galvanometer swings,

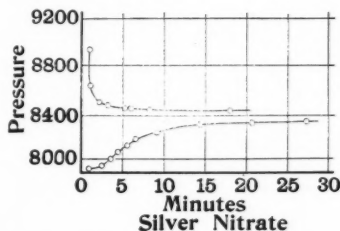


FIGURE 1. The rate at which pressure rises or falls toward equilibrium for Silver Nitrate at 75°.

and the null position is indicated when the cross hair passes the zero mark. Furthermore, by setting the slider at a mark and reading when the galvanometer passes zero, the accuracy of the readings is greatly improved. With a magnifying glass the slider may be set on a division within perhaps 1/50 mm., whereas the position of the slider, if between divisions, cannot be estimated to better than 1/10 mm. The sensitiveness of the galvanometer was such that the mirror magnified the motion of the slider four times. Of course the battery current was chosen so small that the circuit could be closed indefinitely with no perceptible alteration of resistance due to heating by the current.

Such measurements give immediately data for two curves at each of several temperatures, showing pressure as a function of time as it rises from below or drops from above. An example of such a curve is

shown in Figure 1, taken from the data for silver nitrate. It is not however, these curves in which we are primarily interested, but the rate at which the transition runs at constant temperature as a function of the distance measured in kilograms from the equilibrium point. The rate at which pressure changes may evidently be found directly from the tangents to curves like those of Figure 1. In practise the readings were made at frequent enough intervals so that the tangents

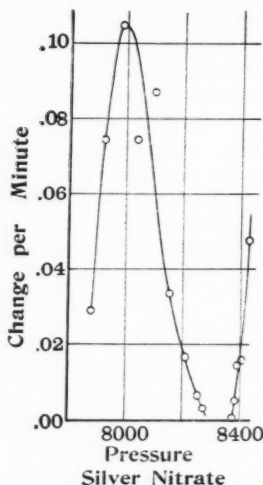


Fig. 2.

FIGURE 2. The slope of the curves of Figure 1, expressed as fractions of the total transition per minute, plotted against pressure. Two of the points on the high pressure branch are beyond the scale of the diagram. The total range of velocity on the high pressure branch is 5000 fold.

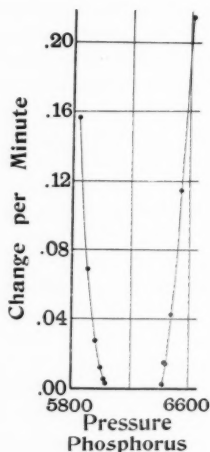


Fig. 3.

FIGURE 3. Transition velocity of White Phosphorus as a function of pressure at 0°.

may be replaced by the secants connecting successive observations. From the rate of change of pressure we can obtain immediately the rate of transition, that is, the fractional part of the complete transition per unit time, if we know the total change of pressure corresponding to the complete transition from one phase to the other. The total change of pressure is given directly by the curves from which the change of volume has been determined. Such a curve of reaction velocity from

above and below is shown in Figure 2; this was obtained directly from the original curve shown in Figure 1.

Curves like these giving the time rate of transformation as a function of pressure were computed from the data and plotted for all the substances for which the time rate could be measured. A few examples of these for different substances are shown in Figures 3, 4 and 5.

To completely present all the data would mean to give all the curves like these, a pair of curves corresponding to every observed

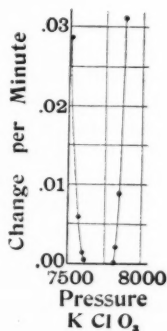


Fig. 4.

FIGURE 4. Transition velocity of Potassium Chlorate as a function of pressure at 200°.

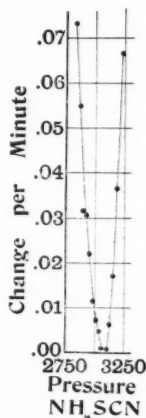


Fig. 5.

FIGURE 5. Transition velocity of Ammonium Sulfoeyanide as a function of pressure at 0°.

pressure and temperature point of the transition curves. Such a complete presentation would demand a prohibitive amount of space, and would be of little significance, because the precise form of the curves depends on the dimensions of the particular apparatus. There are, however, certain features common to all the curves which will be discussed here. By making abstraction of these essential features, each curve may be represented by a single point. The various representative points for a single substance may then be collected into a single diagram, and curves drawn through them. To every transition curve there corresponds, therefore, a pair of curves giving the main

features of the transition velocity curves at each point of the transition curve. The following discussion of the transition velocity curve will make plain what the essential features for comparison are, and how it is possible to represent each curve by a single point.

The four transition velocity curves of Figures 2, 3, 4, and 5 are typical of all. These curves are all similar in appearance except for the hook on the rising pressure branch for AgNO_3 . This hook is connected with the formation of nuclei of the new phase; it is obvious that immediately after formation of the nuclei the growth of the new phase is less rapid than it is after the surface of separation has had a chance to become fully developed. It is probable that all the velocity curves have this hook in the initial stages, but in most cases it was not possible to observe it. In this discussion we confine our attention to the parts of the curve beyond the hook. With this restriction, all four curves are essentially similar. It is in the first place evident that the speed of reaction becomes rapidly greater at pressures increasingly remote from the equilibrium pressure. One could not of course, expect otherwise. This means that some special convention is necessary to give any meaning to the term "*the* velocity of a transition." Such a convention is suggested by the curves themselves. What we mean by a rapid transition is one which increases greatly in speed for a slight shift of pressure away from the pressure of equilibrium. In this sense, therefore, a transition is more rapid if it is represented in Figures 2-5 by a steeper curve. Or stated conversely, a "rapid reaction" in this sense is, paradoxically, one that stops rapidly. This so-called "speed" is really the pressure acceleration of speed. It is natural, therefore, to take the slope of the reaction velocity curve as the measure of the speed of the transition. Throughout the rest of this paper, the acceleration, measured in this way, will be taken as the "speed." This would give a perfectly definite result if the curves were straight lines, but this is not the case. What is more, it does not seem possible to set up a single type of equation which shall be satisfied by all the curves. The most interesting feature of the curves, however, and that least affected by accidental properties of the rest of the apparatus, is the limiting slope when the velocity of transition becomes zero. This limiting slope is evidently to be obtained by extrapolating the curves until they cross the axis, and drawing the tangent at the point of crossing. The numerical value of the limiting slope of the tangent (the acceleration or "speed") expressed as fractional change per minute per kgm. per cm^2 , is one of the essential features referred to above. Corresponding to curves like those of Figures 2-5, there are

two values, therefore, for the limiting transition acceleration, those with rising and falling pressure, and these two values may be plotted as points in another diagram.

It is evident from the diagrams that there is very little possible ambiguity as to the way in which the curves should be extrapolated to the axis. The range of velocities covered by the readings is very wide, and it was possible to approach very close to the axis in nearly every case. In several cases the lowest observed velocity was 5000 times less than the greatest. That the character of the velocity curves is such as to allow this extrapolation is an important fact that will be referred to again in the discussion. One consequence of this is, however, to be insisted on here. The points at which the extrapolated curves for rising and falling pressure at the same temperature cross the axis are not the same. This is particularly evident in Figures 3 and 4 for phosphorus and KClO_3 . This means that there is a pressure range within which the reaction will not run at all, even when the two phases are in contact with each other. This range may be called the "region of indifference." Now as a matter of fact the probability is that this statement is not rigorously true; in at least one case it was possible to just detect the progress of the reaction within the limits of the "region of indifference." In another case just as careful search failed to detect any progress of the transition within the region. This was on the I-II curve of TlNO_3 at 3100 kgm. In any event the velocity within this region must be so small as to belong to phenomena of quite a different order. Thus in the best marked case, that of carbamid, the curve plotted for a range of transition velocities of 1000 fold was of exactly the character of those shown above, indicating unambiguously an extrapolated pressure of zero velocity, but below the lowest measurable point the curve apparently turns and runs along nearly parallel to the axis. This means that if Figures 2-5 were drawn on a scale one meter long, the curves might turn abruptly and run along the axis at less than 1 mm. distance. Although it was not possible to measure the rate of transition within the region it was possible to state that it was of the order of 0.00002 parts per minute. The reaction would not, by its own progress, carry the pressure into this region in practical limits of time. Pressure had to be artificially shifted into this region and the subsequent reaction observed. Various special precautions were necessary in these readings because of the extreme minuteness of the effect. In view of the great difference in order of magnitude, it seems justifiable to suppose that the mechanism involved on the two parts of the curve is different. In the later dis-

cussion I shall make the suggestion that the velocities as ordinarily measured are the velocities of a surface of separation, whereas the minute velocities which are just detectible in some cases are due to the transition running at corners or edges separating one phase from the other. For our present purposes we shall neglect these very small velocities, and discuss without reserve the "region of indifference" as if the reaction velocity were mathematically zero within this region. The width of this region is evidently another datum of significance to be obtained from the velocity curves. It varies greatly from substance to substance, and also varies greatly with pressure and temperature along the transition curve of the same substance. By collecting into a single diagram the widths of the indifferent region for the same substance, we obtain curves showing the width of the region as a function of pressure or temperature along a transition line. In the following these curves are given.

The data for individual substances follow. These comprise curves for the limiting acceleration from above and below, and width of the band of indifference, plotted against equilibrium pressures on the transition line, together with such comment on individual peculiarities as may be necessary. In a number of cases, fragmentary data have been collected, not sufficient to collect into curves. These isolated values are also given.

DATA FOR INDIVIDUAL SUBSTANCES.

PHOSPHORUS.—The transition curves for the two varieties of white phosphorus were given in an earlier paper (C) of this series. The transition velocity data were determined at that time, but were not published. Figure 6 shows the transition accelerations both from above and below, as a function of pressure on the equilibrium line (the temperature range is from 0° to 68°), and in Figure 7 the width of the band of indifference is shown. The observed reaction velocities cover a range of 150 fold. It is to be noticed that the acceleration is greater with falling than with rising pressure, that it is greater at the lower pressures and becomes nearly constant at the higher pressures, that the band of indifference passes through a minimum and becomes rapidly greater at the higher pressures, and that it does not run parallel to the velocity curve.

AMMONIUM SULFOCYANIDE.³—The limiting accelerations from above and below are given in Figure 8. The results are somewhat irregular;

³ E, p. 72.

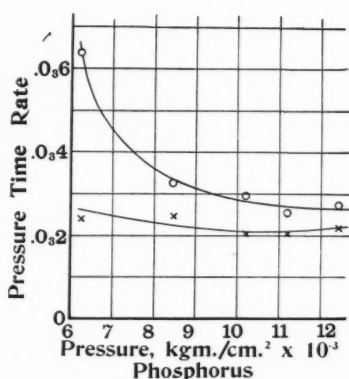


FIGURE 6. The pressure acceleration of the velocity of transition at zero velocity as a function of pressure along the transition curve of the two modifications of White Phosphorus.

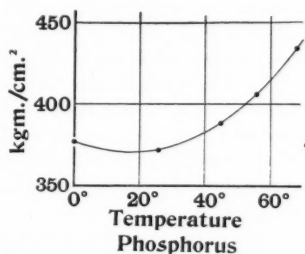


FIGURE 7. The breadth of the band of indifference between the two modifications of White Phosphorus as a function of temperature along the transition line.

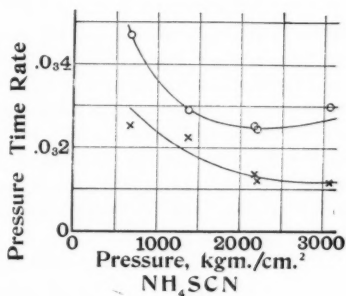


FIGURE 8. Ammonium Sulfoeyanide. The pressure acceleration of the velocity of transition at zero velocity as a function of pressure along the transition line.

it is certain, however, that the reaction with falling pressure is the more rapid, and that in general the reaction becomes slower at the higher pressures. This seems natural when we recall that this transition is of the ice type, higher pressures corresponding to lower temperatures. The band of indifference is very narrow, too narrow to accurately measure. It seems, however, to increase regularly in width with increasing pressure, from about 15 kgm. at a pressure of 680 kgm. to 40 kgm. wide at 3080 kgm.

CARBON TETRABROMIDE.⁴—Observations at only two temperatures were made, on the II-III curve. At 176.6° the accelerations from above and below were 0.00076 and 0.00038 parts per minute per kgm. respectively, and at 152°, 0.00052 and 0.00069. The reversal in order of magnitude is probably not genuine; because of decomposition these results can at best give only the order of magnitude. The band of indifference was 50 and 90 kgm. wide at the two temperatures respectively; as is normal, the width is greater at the lower temperature and lower pressure.

URETHAN.⁵—Measurements were made at only one point, at 0° for the transition I-III. The accelerations were 0.000088 from above and 0.000060 from below, rather slower than the usual. In the preceding paper mention has already been made of the curious behavior of the band of indifference, that it is wider on the I-II and III-II curves at temperatures above the triple point than it is on the I-III curve below the triple point.

CAMPHOR.—The transition data of this substance has not yet been published⁶; it is fairly complicated and contains six modifications. The only one of the transitions with a change of volume large enough so that the time rate could be measured is II-III. The transition line runs from approximately 23° and 2800 kgm. to 115° and 11900 kgm. with little curvature. The accelerations on this curve are shown in Figure 9. The reaction is more rapid with falling than with rising pressure (the reversal at 6000 is probably not genuine) and grows more rapid at the higher pressures. The breadth of the band of indifference is shown in Figure 10; the band becomes rapidly wider as the pressure increases. It is remarkable that the reaction velocity should increase at the same time that the limits of indifference become wider.

CAESIUM NITRATE.⁷—There are two modifications, the transition

⁴ E, p. 90.

⁵ E, p. 118.

⁶ See, however, F for the general nature of the phase diagram.

⁷ G, p. 587.

line running nearly linearly from 153.7° at 1 kgm. to 207.1° at 6000 kgm. This substance seems to be normal in every way, and the measurements on it are as satisfactory as any. The transition accelerations are shown in Figure 11; the velocity is always greater from above and

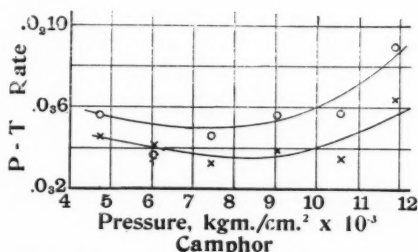


FIGURE 9. Camphor. The pressure acceleration of the velocity of transition at zero velocity as a function of pressure along the transition line between the modifications II and III.

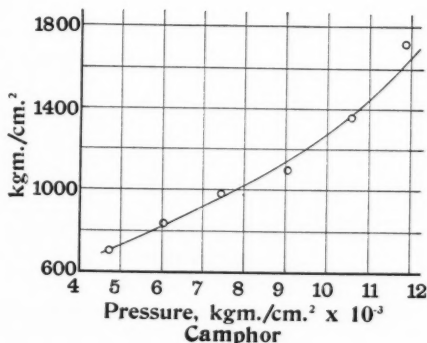


FIGURE 10. Camphor. The breadth of the band of indifference between the modifications II and III as a function of pressure along the transition line.

decreases with rising pressure. The band of indifference was inappreciable in width at the two lower points, but at 5500 suddenly jumped to 90 kgm.

SILVER NITRATE.⁸—There are two modifications, the transition is of the ice type, and there is a sudden and remarkable increase of curvature of the transition line near 7000 kgm. The transition acceleration curves are shown in Figure 12 and the breadth of the region of

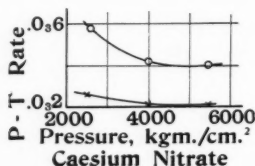


FIGURE 11. Caesium Nitrate. The pressure acceleration of the velocity of transition at zero velocity as a function of pressure along the transition line between the two low temperature modifications.

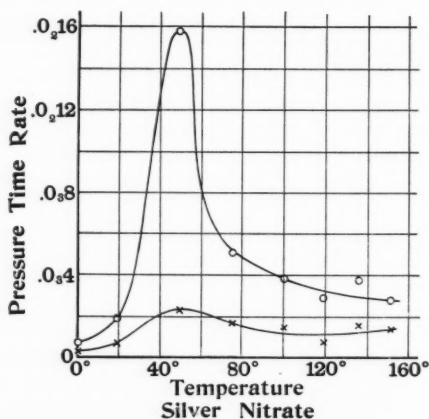


FIGURE 12. Silver Nitrate. The pressure acceleration of the velocity of transition at zero velocity as a function of temperature along the transition line. The position of the maximum corresponds to a region of rapid change of direction of the transition line.

indifference in Figure 13. The acceleration with falling pressure is greater throughout; the region of increase of curvature of the transition line is mirrored by a remarkable increase of reaction velocity.

AMMONIUM NITRATE.⁹—It was possible to make measurements on several of the transition curves. The limiting accelerations are shown in Figure 14 and the width of the bands in Figure 15. A single

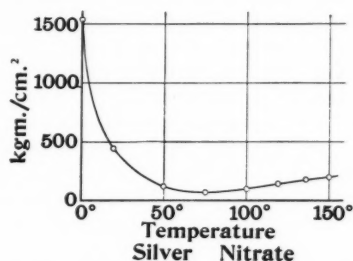


FIGURE 13. Silver Nitrate. The breadth of the band of indifference as a function of temperature along the transition line.

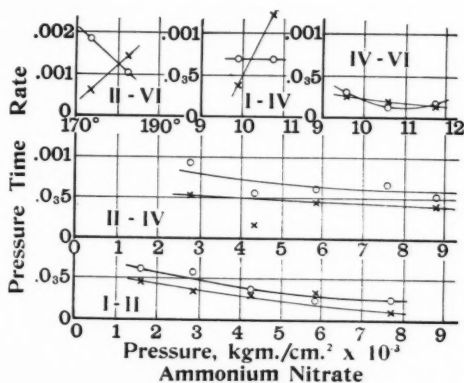


FIGURE 14. Ammonium Nitrate. The pressure acceleration of the velocity of transition at zero velocity as a function of pressure or temperature along the transition lines of the several modifications. Observe the change of abscissa for II-VI.

observation on the II-III curve at 67° gave a band width of 115 kgm. and limiting accelerations of 0.0013 and 0.00026 with falling and rising pressure respectively. The reversal of the acceleration,

⁹ G, p. 605.

that with rising pressure in some cases being greater, is an interesting feature of these curves, but may be due to experimental error. The sudden increase of the width of the band of indifference for II-IV from zero to a fairly large value at the higher pressures is an interesting effect, but is not unique to this substance; CsNO_3 affords another example.

CARBAMIDE.—This has three modifications, but only two transition curves available for measurement.⁶ On the upper of these two curves above 100° , the transition is extraordinarily rapid, much too rapid to measure, and the width of the band is sensibly zero. In no case was the difference of pressures reached from above and below more than 5 kgm., and in many cases there was no appreciable differ-

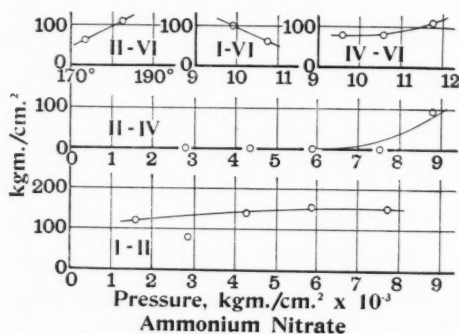


FIGURE 15. Ammonium Nitrate. The breadth of the band of indifference between the several modifications as a function of pressure or temperature along the transition lines.

ence. On the lower curve between 0° and 100° for the transition I-III the reaction was slow enough to measure. Three different experimental arrangements were used; the carbamide was either rammed tightly into a steel cup under mercury or submerged in loose pieces under mercury, or rammed into a light steel shell and pressure transmitted by kerosene. There is a very slight dissolving action of the kerosene, not sufficient to vitiate the pressure-temperature values, but sufficient to slightly round the corners, and so vitiate the measurements of the time rate. This was one of the few cases in which a restraining action of the steel shell was noticeable; the reaction accelerations were less and the width of the band of indifference greater

when the carbamide was restrained under mercury than when it was free. This is merely another manifestation of some peculiarity of behavior during the transition that will be further commented on in the paper containing the equilibrium data.

There are measurements at only three points with the carbamide free under mercury; the results for the transition acceleration are shown in Figure 16 and for breadth of the band of indifference in Figure 17. The acceleration with falling pressure is greater than

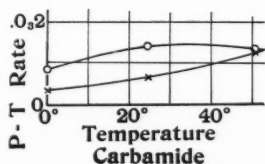


FIGURE 16. Carbamide. The pressure acceleration of the velocity of transition at zero velocity as a function of temperature along the transition line between I and III.

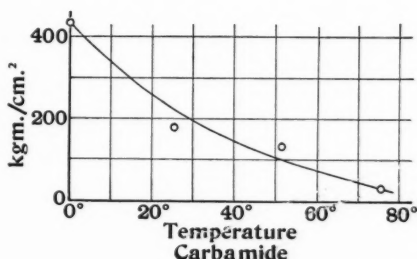


FIGURE 17. Carbamide. The breadth of the band of indifference between the modifications I and III as a function of temperature along the transition line.

normal, and both accelerations are greater at higher pressures. These data suggest, however, and the suggestion is much strengthened by the other discarded data, that at temperatures between 65° and 100° the acceleration with rising pressure becomes greater, and that the acceleration with falling pressure may even pass through a minimum, to rise again. This may have some connection with the third phase. The band of indifference becomes rapidly less in width at the higher

temperatures, and becomes inappreciable above 80° . In Figure 16 the point obtained at 75° with the restrained carbamide has been included; this is legitimate if this point is regarded merely as setting an upper limit.

It has already been mentioned that carbamide was the substance which shows a reaction velocity of a smaller order of magnitude at points within the extrapolated region of indifference. This phenomenon was observed at 0° . It was possible to detect motion at points only 65 kgm. apart, whereas the extrapolated width of the indifferent band was 435 kgm.

ACETAMIDE.—The results are to be published in the following paper.⁶ Measurements of the rate were made only with a specimen which was afterwards found to be impure. The results are too irregular for graphical representation. The acceleration with falling pressure is throughout about twice as great as that with rising pressure, and increases markedly with rising temperature along the transition line. The width of the indifferent band falls greatly with increasing temperature from about 700 kgm. at 25° to about 70 kgm. at 100° . Above 100° , although no measurements were made on the pure specimen the band of indifference remained of appreciable width, perhaps of the order of 50 kgm.

POTASSIUM CHLORATE.—A large number of measurements were made on this substance,¹⁰ but it does not pay to reproduce them in detail because the effects were different in character than for other substances. It has already been stated that at the lower temperature the region of nucleus formation was so extensive as to cover the entire region of observation, so that the pure surface growth could not be observed. At higher temperatures, however, the phenomena become like those for normal substances. The acceleration with falling pressure is greater than with rising, and both accelerations become greater at higher temperatures. There is a well defined band of indifference which becomes narrower at the highest temperature. That there should be a band of indifference at all shows that the effect of rising temperature is much less in increasing the facility of nucleus formation than in increasing surface transition velocity.

¹⁰ E, p. 78.

DISCUSSION.

A simple interpretation of the results is complicated by several obscuring factors, which we will first discuss. There is, in the first place, the effect of the heat set free during the transition. The effect of this is that the temperature at which the transition is running is not the observed temperature of the bath, but differs from it by an unknown amount depending on the magnitude of the heat of transition, the transition velocity, and the thermal conductivity of the surrounding envelope. If the transition is very rapid, the measured rate may be entirely controlled by the rate of dissipation of the latent heat, the two phases being always under equilibrium conditions at the momentary actual temperature of the interior. As heat is conducted away from the interior, the pressure so changes as to assume the value appropriate to the temperature of the interior, and it is this rate of change of temperature which is really measured. This is preëminently the case on a melting curve. Of course it is not possible to carry the solid any distance at all into the domain of the liquid, and the apparent rate of change of pressure is only the rate at which pressure follows the return of temperature along the equilibrium line. The reverse displacement, that of the liquid into the domain of the solid, is possible to carry out, because liquids may be subcooled. But even in the reverse case, the latent heat of freezing is so large, and its rate of dissipation is so slow compared with the rate of crystallization of the liquid, that the apparent rate is governed by the thermal conductivity. The result is that the apparent rate of melting of most solids is exactly the same as the apparent rate of freezing. Figure 18 for mercury shows an example of this. In some cases, however, the velocity of crystallization is unusually slow, so that an appreciable fraction of the latent heat is conducted away during the freezing, and it may be possible to detect the difference of velocity between melting and freezing. Figure 19 shows such results for benzophenone. If the conductivity were perfect, results of this character would be shown by all liquids; the rate of melting would be infinite and the rate of freezing would be a different characteristic rate for every substance. As a consequence of this large disturbing factor, it has not been worth while to try to collect any data for the rate of melting or freezing under pressure.

Slow thermal dissipation is evidently going to be a disturbing factor also in the case of solid transitions, but to a much less degree than for

melting. There are two reasons; the latent heat of transition is usually very much less than that of melting, and the velocity of a solid transition is usually less than that of melting or freezing. The thermal effect is, however, entirely absent only when there is no heat of transition; that is, when the transition curve is vertical. Several substances approach rather close to this ideal.

The unavoidable result of slow rate of dissipation of latent heat is

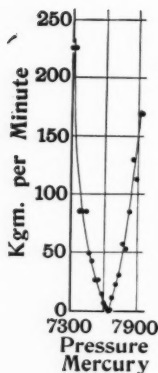


Fig. 18.

FIGURE 18. The time rate of change of pressure as a function of pressure during the melting and freezing of mercury under pressure at 0° . The symmetry of the curves is due to slow thermal conduction.

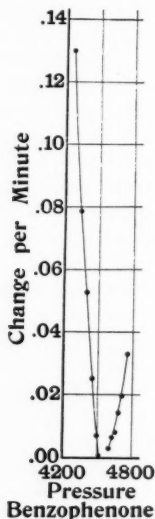


Fig. 19.

FIGURE 19. The rate of freezing or melting of benzophenone, expressed as fractional parts of the total change per minute, as a function of pressure. The steeper curve at the left shows that melting is more rapid than freezing.

that only a relative significance can be attached to these results. There are other factors also which rule out the possibility of an absolute interpretation. The effect of the manner of the mechanical constraint of the specimen is to be considered. Most of the specimens were originally in the form of dry powder or small crystals; these were

pounded dry into a thin steel shell about 6 inches long and 11/16 of an inch in diameter, open at both ends, and perforated on the sides with small holes to allow ready access of the liquid transmitting pressure throughout the entire mass. Several measurements were made to detect a possible restraining action of this shell, and in nearly every case none could be detected, but the fact that some slight effect could be detected in one or two extreme cases where the lateral holes were discarded and the shell left closed on the bottom end leaves open the possibility of a very slight effect in all cases. The state of subdivision of the substance must also have an effect. If it is in the shape of a fine powder compacted together by the hammer, the new phase must spread somewhat less rapidly from grain to grain than it would in a homogeneous fused mass. Some of the substances were fused into place, but even these always developed cracks during use, thus introducing the same element of uncertainty. Furthermore, there may be a slight specific effect exerted by the liquid transmitting pressure. This liquid penetrates through all the crevices, and might even in some cases exert a catalytic effect, although this extreme is unlikely. Usually pressure was transmitted by kerosene, but mercury was used for most organic substances. In the case of KClO_3 a greater reaction acceleration was found with mercury for the medium than with kerosene. This may be in part a thermal conduction effect. It is also likely that in some cases slight impurity may affect the transition velocity, although its effect on other properties might be inappreciable.

These considerations suggest the use to which these observations can legitimately be put. They must not be used in calculating the absolute rate of growth of any one phase at the expense of another, they may be used cautiously and with great reserve in comparing the velocity under similar conditions of different materials, since the form of apparatus was nearly constant for all these measurements, and they may be advantageously employed in finding the variation of rate of the same substance under different conditions of pressure and temperature and direction of transition. This last is the use to be made of them in this paper.

We now have to inquire just what it is that we have been measuring. It is common knowledge that there are two distinct processes involved in either crystallization from a melt or in the formation of new polymorphic phases. These are: first the formation of nuclei of the new phase, and secondly a surface growth of the new phase, starting from the nuclei. In the case of two solids, nuclei of the new phase are formed only when temperature or pressure is raised or lowered a

suitable amount away from the equilibrium point. Of course no hard and fast bounds can be set to this region within which nuclei are not formed, because at any point the formation of a nucleus is a matter of chance, but within the limits of time within which laboratory experiments can be made it is safe to say that there is a region on *both* sides of the equilibrium point within which new nuclei will not be formed. By working only within this region, the phenomena of surface growth may be observed separated from the disturbing effect of nucleus formation. This is an essential distinction between a polymorphic transition and melting. With only a very few possible exceptions a solid cannot be carried any distance into the domain of a liquid without the formation of liquid nuclei, so that it is impossible to observe pure surface growth of a liquid into a solid.

The experimental conditions were such that the measurements of this paper are almost entirely concerned with the surface growth and not with formation of nuclei. It will be recalled that the method was to increase the pressure on one phase until a nucleus of the new phase appeared; and then to observe the rate of fall of pressure. All the internal evidence makes it probable that in most cases only one nucleus is formed, and that what is observed is the rate of advance of a single surface of separation. In support of this statement it is in the first place evident that as soon as a single nucleus is formed the progress of the reaction makes the formation of others much more difficult, and since nucleus formation is a matter of chance it is very unlikely that two nuclei are formed simultaneously. In the second place, the regularity of the points, always lying on smooth curves, makes it very probable that the conditions are always comparable; if sometimes we were measuring the rate of growth of surfaces starting from three nuclei and at other times from only one, we could not expect smooth curves. This is a matter of considerable importance for our interpretation of the results. We have noticed that the transition acceleration with decreasing pressure is in practically all cases greater than with rising pressure. Now this might be either because the surface of separation at a constant distance from equilibrium moves more rapidly with decreasing pressure, or because more nuclei of the high pressure phase are formed than of the low pressure phase, so that with decreasing pressure we are observing the rate of advance of more surfaces than with increasing. This particular point may be settled experimentally. If during a reaction with rising pressure we artificially raise the pressure into the region of the reverse transition, but not into the region of the formation of nuclei, the ensuing fall of

pressure is due to a reversal of direction of transition at exactly the same surfaces which we had been previously observing. This was tried on several occasions, and no difference found between experiments under these and the usual conditions; the transition velocity with falling pressure was in all cases greater. It is therefore, very probable that in most cases only one nucleus was formed. But one nucleus would give rise to two surfaces, travelling in opposite directions along the cylindrical container. The limiting accelerations listed above were usually observed when between 50 and 90% of the substance had been transformed. If the nucleus were formed at random throughout the mass, this limiting acceleration would sometimes be observed with one and sometimes with two surfaces. But if the original nucleus were always formed near one end of the tube, one of the surfaces of separation would have run to the end of the tube and disappeared, so that the final observations would always be on one surface only. The regularity of the results makes it almost certain that this is what happened. It is, in any event, to be expected that nuclei will be formed near the ends in preference to the central portions, because the first effect of change of pressure would be felt near the open ends.

It was not possible to detect any connection whatever between transition acceleration and the total quantity of the substance that had been transformed. The data were of course at hand from which the total fraction of transformed material corresponding to each limiting acceleration could be determined. These fractions were written down against every point of all the curves plotted, and showed an utterly random distribution. This of course is what would be expected if the measurements are actually of the rate of advance of a single surface; the rate of this surface will not involve its position in the cylindrical tube.

Although the data of this paper are almost entirely concerned with the surface growth, some comment is called for on phenomena connected with nucleus formation. In some cases the observed pressure change did not initially assume a high velocity and decrease regularly, but at first increased, passed through a maximum, and then decreased. This is shown in Figure 2 for AgNO_3 . It is without doubt due to the fact that the surface of the freshly formed nucleus has not yet attained the maximum extent allowed by the container; the total rate of transformation of one phase into the other is less because the small extent of the surface at which growth occurs more than compensates for the rapid linear advance of the surface. This phenomenon is probably

exhibited by all substances, but for most substances the rate of advance of the surface in the region of nucleus formation is so rapid that it was not possible to make any measurements. The existence of the effect was established for AgNO_3 , KClO_3 , Acetamide, and Carbamide. The effect was in most cases shown only on the rising branch, on which the velocity was less, thus making it easier to observe. Carbamide, however, showed two examples on the falling branch, and acetamide one.

The question of the extent of the region in which no nuclei are formed is of interest. As has been said, no fixed limits can be assigned to this region, but the formation of a nucleus is a matter of chance. It is to be expected, therefore, that occasionally nuclei will be formed outside of the usual region. The effect of such a freshly formed nucleus will be to add more surfaces of separation, and so to increase the measured rate. Such effects were found for two substances, AgNO_3 , and KClO_3 . Several of the rate curves for AgNO_3 with rising pressure showed a secondary maximum or a region of arrest, to be explained in this way. The effect was so pronounced with KClO_3 that these secondary maxima appeared persistently throughout the entire region of observation with rising pressure at 0° . It is evident, therefore, that different substances differ greatly in the sharpness of the boundaries of the region of nucleus formation. For most substances the boundary is so sharp that no chance nuclei were ever formed in the region of observation. Furthermore with AgNO_3 and KClO_3 the boundary of the region at pressures above equilibrium was very much sharper than at pressures below; no secondary maxima or regions of arrest were observed with falling pressure. In the case of AgNO_3 the boundary was sufficiently sharp so that the extra velocity due to additional nuclei did not affect the limiting acceleration; the extra surfaces due to the extra nuclei having merged into the other surface before the final reading. This was shown by the regularity of the limiting accelerations, which lie on a fairly smooth curve, irrespective of whether there had been a secondary maximum or not. The disturbing effect with KClO_3 , however, extended throughout the entire region of observation at 0° , so that it was not possible to establish any limiting acceleration. At higher temperatures the boundary for KClO_3 became much sharper and the curves became normal in every respect, as shown by Figure 4.

The question of the sharpness of the boundary of the region of nucleus formation is an interesting one for investigation, both experimental and theoretical. It has received little attention, but would

seem capable of giving information about the mobility of the molecules in a crystal, or the number that must fall together in the right position in order to start a nucleus. It is probable that the formation of even a nucleus is a rather complicated matter. If nothing more were demanded than that two or three molecules come together in the right position, it is difficult to see why the region of nucleus formation should have any boundaries. The process may be something like this; two or three molecules fall together to form the beginning of the nucleus. These molecules by their orientation tend to attach other molecules to them in the same orientation; this tendency is greater at points farther removed from equilibrium. This process of agglutination until a full fledged nucleus is formed, is somewhat different from the ordinary surface growth. In the early stages there are disintegrating forces due to the comparatively small number of elements involved and the effects of surface tension, which vanish under the conditions of surface growth proper.

One of the most important results of these measurements is the establishment by an extrapolation that there is a region of no appreciable velocity. It has been stated that there may be actually some velocity in this region. The question arises, therefore, as to how justified the extrapolation is which entirely neglects this very small effect. The answer is that practically, except in one case, there was never the slightest doubt. Theoretically the possibility must be recognized that the velocity curves may turn gradually at the bottom and so vitiate the extrapolation, but practically, on diagrams of about ten times the scale of the published figures, there was no such effect. The only exception was KClO_3 at low temperature, and it has already been stated that for this substance the formation of nuclei was abnormally persistent over a wide range, and this effect is entirely competent to explain the character of the curves. So even in the case of this one exception, we have no reason to believe that the small reaction within the region of indifference would vitiate the extrapolation. One is the more strengthened in the belief that the small residual effect is due to a distinct mechanism when one considers that there must be corners and edges as well as surfaces of separation of the two phases, and that at corners and edges just this sort of an effect would be expected because of the lack of perfect homogeneity. Furthermore, observations of this small residual rate were made only after pressure had been carried artificially into the indifferent region. Under these conditions corners and edges must have been more numerous than if the reaction had been allowed by its own progress to enter this region,

and therefore the observed transition velocity is very possibly greater than if the reaction had been allowed to run its natural course. In the following, this small residual effect will be entirely disregarded, if indeed it exists in most cases, as being an extraneous effect.

The general behavior of the acceleration curves next calls for comment. One feature common to nearly all the curves is that the acceleration with falling pressure is greater than with rising. This is what one would expect; that reaction runs more rapidly which is pushed by the external pressure. There may be a few exceptions, however, as in the case of NH_4NO_3 .

With regard to the variation of the acceleration along the transition curves we may have either increasing or decreasing acceleration at the higher temperatures. It is to be recognized that on a normal transition curve there are two opposing tendencies; increase of pressure would be expected to decrease the transition acceleration, because of increase of viscosity, while increasing temperature would increase it. Phosphorus is a well marked example of decreasing acceleration, and camphor of increasing. The curves for AgNO_3 are remarkable; the acceleration passes through a maximum, much more pronounced for falling than for rising pressure, in the region of the rapid change of direction of the transition curve. It has already been stated that this is a region of anomalous behavior of other physical properties also. The accelerations with rising and falling pressure are usually affected in the same way as we move along a transition line, but the magnitude of the effects may be different, and in exceptional cases possibly the signs may be unlike.

The behavior of the region of indifference next concerns us. It is first to be noted that the apparent equilibrium within the region of indifference is somewhat different in its nature from the so-called "false equilibria" with which we are familiar in such cases as diamond and graphite or hardened steel. The usual explanation of the failure to react in such cases is that one of the phases has been cooled so far below the temperature of transition that the velocity of transition has become inappreciable because of the enormously increased viscosity. A similar example is afforded by those liquids which may be subcooled so far as to become glassy. In the cases described in this paper, however, the reaction does not run when two phases are in contact at only a slight distance from the equilibrium temperature. Such immobility cannot be a viscosity effect, because at lower temperatures, where the viscosity is greater, the reaction may run with high velocity.

Phenomena consistent with these have been observed before. In

the case of CBr_4 , Wahl¹¹ has observed optically that there is a region within which the reaction could not be observed to progress. This region was narrow, could be rather sharply observed, and was of approximately the same width as I have found above. The phenomenon has also been observed by Tammann¹² for the two varieties of phenol at low temperatures. I am not aware, however, that anyone has ever before actually measured the velocity at points outside the region and shown by an extrapolation that there is really a region of no appreciable velocity. I have been able to make such measurements only because of an apparatus absolutely without leak.

The width of the region of indifference varies at different points on the equilibrium curve. We should expect rising temperature to decrease the width of the region, and rising pressure to increase it. With NH_4SCN the region increases in width with falling temperature and rising pressure; the width is about twice as great at 0° as at 67° , although the width is in either case comparatively slight. CBr_4 shows a decreasing width with rising pressure and temperature; the effect of rising temperature here overbalances the effect of rising pressure. The band of indifference of Urethan decreases strikingly with rising temperature on all three transition curves; this has been described more fully in a preceding paper.¹³ Phosphorus shows on the whole an increase of width with rising pressure and temperature, but has a flat minimum which is of interest. This points to a preponderating effect of temperature at low pressures, but at the higher pressures the retarding effect due to increased pressure overbalances the acceleration due to rising temperature. In a previous paper it was stated that the width of the band for phosphorus was inappreciable,¹⁴ but this is now seen not to be true. The previous statement was deduced from a diagram like that of Figure 1; the advantage of the diagrams used in this paper is obvious. Phosphorus shows that there is no necessary connection between the width of the band and the acceleration of transition. The band becomes wider with increasing pressure and temperature, but the transition acceleration increases also. CsNO_3 shows an effect similar to phosphorus; at 177° and 190° the region of indifference has no appreciable width, but at 202° the width is 100 kgm. This is doubtless the effect of increasing pressure, as opposed to the effect of increasing temperature. AgNO_3 is interest-

¹¹ W. Wahl, Trans. Roy. Soc. (A) 212, 137 (1912).

¹² G. Tammann, ZS. phys. Chem. 75, 75-80 (1910-11).

¹³ E, p. 122.

¹⁴ B, p. 185.

ing in this connection, as it is in many others; the width of the region, shown in Figure 13, passes through a minimum. On the equilibrium curve, temperature rises as pressure falls, as for NH_4SCN , so that one would expect a steady increase of width with rising pressure. The minimum seems to have some connection with the locality of the sharp bend of the equilibrium line.

The fact that there is an indifferent region introduces a possible error into determinations of the equilibrium values of pressure and temperature. Of course the fact that there is a region within which the reaction does not run does not prevent our attaching a definite meaning to the equilibrium coördinates. These are to be defined thermodynamically as the points at which the thermodynamic potentials of the two phases are equal. To apply this definition demands that at least at one point the reaction run without sticking. The error in the equilibrium coördinates due to the region of indifference is also of course operative at atmospheric pressure. In most cases it is only possible to shut the equilibrium temperature between an upper and a lower limit. The limits vary greatly for different substances; there are many solid transitions which are apparently as sharp as a melting point.

The actual point of equilibrium, defined thermodynamically as above, may be situated, as far as we can tell, at any point within the region of indifference. In all the preceding work, the equilibrium point has been assumed to be in the middle of the indifferent band. In most cases this can lead to only very small error, because the width of the band is small compared with the total pressure. But in a case like that of AgNO_3 at 0° the error from this cause may become appreciable. An attempt to correct the equilibrium point by displacing it from the center in proportion to the transition velocities from above and below might lead to better results, but we could not be sure of them, because we have seen that there is no necessary connection between the width of the band and transition velocity. It is conceivable that the true equilibrium point might lie on that side of the center of the band toward the smaller velocity.

Before proceeding to the final part of the discussion, which will be occupied with an attempt to find the implications as to mechanism of these new facts, it will pay to very briefly recapitulate the nature of the facts. There are two cardinal facts; in the first place there is a region of indifference surrounding the equilibrium point within which the transition does not run even when the phases are in contact, and secondly the transition velocity at points equally distant from the

equilibrium point is in nearly every case greater with falling than with rising pressure. There is no uniformity among different substances as to the direction of variation of either the width of the band of indifference or of the transition velocity with rising temperature along the transition line.

The first conclusion to be drawn is that the mechanism of a polymorphic transition cannot be the same in nature as that of a vaporization. Equilibrium between a liquid and its vapor is a dynamic equilibrium in which two independent processes are involved; molecules of the liquid leave the surface of the liquid and enter the vapor phase, and molecules of vapor impinge on the liquid surface and enter the liquid phase. At those pressures and temperatures for which these two streams of molecules in opposite directions each carry the same

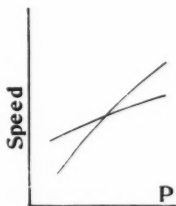


FIGURE 20. Curves showing at constant temperature the probable velocity of vaporization of a liquid or condensation of its vapor as a function of pressure. The equilibrium pressure is that at which the two curves cross.

quantity of matter per unit time, there is equilibrium between liquid and vapor. The velocity of these two streams of molecules may be represented as a function of pressure at constant temperature as in Figure 20. The equilibrium pressure is located at the point of intersection of the two curves. It is immediately evident from the diagram that at points near the equilibrium point the velocity of vaporization or of condensation is equally great at points equidistant from the equilibrium point on either side.

Each of the two cardinal facts mentioned above shows that this cannot be the mechanism of polymorphic transition. If such a mechanism were consistent with the existence of a region of indifference, the curves for velocity of transition in opposite directions would have to be of the form in Figure 21. Further, if the mechanism were consistent with unsymmetrical transition velocities on opposite

sides of the transition point, when there is no appreciable region of indifference, one at least of the transition velocity curves must have a bend at the equilibrium point, as shown in Figure 22. But the curves of both Figures 21 and 22 involve non-analytical singularities of a kind that we are not willing to admit in our physical phenomena, at least not on this scale of magnitude.

The fact that polymorphic equilibrium is not a dynamic equilibrium is significant with respect to the random distribution of velocity of temperature agitation among the molecules. In a vapor there is almost certainly, and in a liquid quite probably, a very close approach to Maxwell's distribution of velocities. In such a distribution there are always some molecules with a velocity so much above the average that they can pierce the transition layer and enter the other phase.



Fig. 21.

FIGURE 21. Hypothetical curves showing what must be the nature of the velocity between two polymorphic modifications in those cases where there is a band of indifference.



Fig. 22.

FIGURE 22. Hypothetical curves showing what must be the nature of the transition velocity between two polymorphic modifications in order to explain asymmetry of velocity in those cases where there is no band of indifference.

The fact of the existence of the region of indifference shows that with polymorphs there are no molecules at the equilibrium point with velocities high enough above the average to pierce the transition layer (or its equivalent) and enter the other phase. That is, in a crystal the random temperature agitation is random only within a restricted range; the velocity never rises above a definite limit. This is certainly consistent with the known definiteness of crystal structure as shown by X-ray photographs. The region within which the velocities are confined in all probability does not have a sharp boundary, but is more or less nebulous at the edges. We recognize that the abruptness of this boundary within which the velocities are confined may vary greatly from substance to substance, and may also vary with the same substance at different pressures and temperatures.

We have ruled out the reciprocal passage of molecules between

polymorphic phases; we must therefore find some other mechanism which will carry the molecules from one phase to the other. As I have mentioned in a previous paper,¹⁵ the fact that the conditions of equilibrium involve the constants of both phases shows that a transition from one phase to another does not take place because the first phase, at the equilibrium pressure and temperature, suddenly becomes inherently unstable, and falls apart into its elements, which then build themselves up into some other arrangement which under the conditions does happen to be stable. The instability of one phase is only a relative instability, into which the properties of the other phase enter. The driving force from one phase to the other is doubtless to be found in a definite orienting force exerted by the one phase on the molecules of the other. The same orienting force comes into play when a crystal separates from solution; there is a field of force like a skin over the crystal which compels the molecules being freshly deposited to orient themselves definitely with respect to the regular assemblage of molecules already laid down. In the same way, when two polymorphs are in contact, each phase reaches into the other and strives to orient the molecules of the other into its own position. Above the equilibrium point the orienting forces of one phase prevail, and below it those of the other. This struggle for mastery between the orienting forces of the two phases is a static rather than a dynamic struggle, like a tug of war rather than a game of tennis.

It is possible to represent graphically some of the counter-play of forces on the molecules. We will go to the extreme of simplification and suppose that at any constant temperature and pressure all possible configurations, whether stable or unstable, of the molecules of a crystal may be defined by a single position coördinate. Corresponding to each arrangement there is a definite potential energy. We plot potential energy against position coördinate. If the configuration is a stable one, the potential energy is a minimum. If the substance has two arrangements of possible stability (polymorphism) there will be two minima, and the lowest one will correspond to the absolutely stable form. At an equilibrium point the two phases are equally stable and the two minima are at the same level. At pressures above equilibrium pressure (at constant temperature) the minimum of one phase becomes the absolute minimum, and vice versa. Such a state of affairs is indicated in Figure 23. Let us now consider the curve corresponding to equilibrium. If a molecule is to pass from the phase

¹⁵ D, p. 108.

I to the phase II, it must pass over the intervening maximum of energy. This passage may take place if the range of irregular thermal agitation is so great that some molecules occasionally possess an amount of energy greater than the average equal to the height of the hill, but otherwise the transition will not take place, even when the phases are in contact. In this way we get a region of indifference.

If there is a region of indifference, its width is fixed by the position of the first curve beyond the equilibrium curve on which the height of the hill can be surmounted by the haphazard temperature agitation, aided by the orienting forces of the more stable phase, which away from the equilibrium point prevail over those of the unstable phase. According to the specific effect of pressure and temperature on the shape of the potential energy curves and on the random distribution

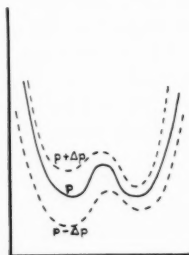


FIGURE 23. Shows at constant temperature the potential energy of position against position coordinate in the neighborhood of a transition point for a substance which has two polymorphic modifications.

of temperature agitation, it is easy to see that the band may become broader or narrower at higher temperatures on the transition line. It is conceivable, although unlikely, that the height of the hill to be surmounted should so increase on both sides of the equilibrium point that the reaction will never run, no matter how far one goes from the equilibrium point. Or the other extreme is more probable, that at points sufficiently far from equilibrium, the hill, together with one of the minima, should totally disappear, resulting in the absolute instability of the corresponding phase. This is Ostwald's labile state, or the unstable portion of James Thomson's isothermal.

The pressure acceleration of the transition velocity is evidently intimately connected with the sharpness of the region of random temperature agitation. If all the molecules once in every few oscilla-

tions receive enough energy to surmount the barrier, the transition is cataclysmic; but on the other hand, is very slow if only once in a while a molecule receives enough energy to slip over. A transition increasing in acceleration with increasing temperature means that the border of the velocity domain becomes sharper at the higher temperature, and a retarded acceleration at higher pressures means a more nebulous boundary. In general the results above do show a more nebulous boundary at higher pressures. One would expect, therefore, that the velocity domain of the phase of smaller volume would have the more nebulous boundary. This is precisely what the greater acceleration with falling as compared with rising pressure means. During the falling pressure transition, the low pressure modification, with the sharper velocity boundary is tumbling over the hill into the lower minimum, and is running with the greater speed.

It is suggested by the figures that in extreme cases, when the intervening hill is low, and the domain of temperature distribution is wide, that not only should there be no region of indifference, but that the equilibrium should be of the nature of a liquid-vapor equilibrium, and should involve equality of streams of molecules in two directions. Such transitions must be of great velocity, and would not be expected to be within the range of these observations. This may perhaps be the nature of the equilibrium in the neighborhood of a triple point between two solids and a liquid, on the upper end of the ice I-III curve, for example.

This analysis does not pretend to be an explanation; it makes no attempt to explain why the various factors vary with pressure and temperature in the way in which we have supposed they may. It is merely an attempt to state the nature of the elements that may enter the problem.

SUMMARY.

The rate at which one polymorphic modification is transformed into another may be measured by the time rate of change of pressure at constant temperature during the transition. Data for the velocity of a number of such transitions are given in this paper. It is probable that all the measurements of this paper have to do essentially with the rate of advance of a single surface separating the two phases. The rate of advance increases rapidly as pressure is displaced from the pressure of equilibrium between the phases. As a rough comparative

measure of the speed of the transition we may use the pressure acceleration of the speed at zero velocity. The acceleration of nearly every transition is not symmetrical with respect to the direction of the transition, but is greater in the direction accompanied by decreasing pressure. Furthermore, there exists for most substances a distinct region on both sides of the equilibrium point within which the transition will not run even when the two phases are in contact. This is the "region of indifference." The acceleration of the transition and the breadth of the band of indifference vary with pressure and temperature along the transition curve; the manner of variation is different for different substances.

It results from these facts that an equilibrium between polymorphs cannot be due to a balance between two transitions running in opposite directions, as is the case for vaporization. This implies that in a crystalline solid the velocities of temperature agitation of the molecules cannot be distributed over a wide range of velocities, as is demanded by Maxwell's distribution law for gases or liquids, but must be confined within a restricted range. The boundaries of this range may be more or less sharp. The sharpness of the boundary is an important factor in determining the acceleration of the transition velocity.

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THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

